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Description

Process for Recovering Argon by Low-Temperature Air Separation

The invention relates to a process for recovering argon by low-temperature separation of air in a rectifying system, which has three rectifying sections that are arranged in series, whereby the first and the second as well as the second and third rectifying sections in each case are connected to one another on the gas and liquid sides, and whereby the second rectifying section has two subsections, which are not connected to one another on the gas and liquid sides and are flushed in a parallel manner, whereby a fluid that contains oxygen and argon is introduced into the first of two subsections and a stream that contains oxygen and argon is removed in the second of the two subsections.

The boiling point of argon is located between the boiling points of oxygen and nitrogen. In the standard low-temperature separation of air by two-stage rectification, the argon accumulates in a middle area of the low-pressure column. For argon recovery, a gaseous fraction, which essentially consists of oxygen and argon, is usually removed from this area. This fraction that is concentrated with about 10% argon is fed to the so-called crude argon column into which a separation of oxygen and argon by rectification is performed. At the head of the crude argon column, argon can be drawn off, and in the bottom thereof, a liquid that essentially contains oxygen is collected that then is returned into the low-pressure column.

In practice, argon purities of over 95% are frequently called for. In the known process, however, a stream that only contains approximately 10% argon is fed to the

crude argon column. To concentrate the latter to the desired high argon purities and to be able to draw off the desired amount of product at the head of the crude argon column, considerable amounts of vapor must be introduced into the crude argon column and rectified in the latter. The cross-section of the crude argon column must be selected in a correspondingly large size, by which considerable investment costs arise.

In particular from the field of hydrocarbon recovery, it is already known to use so-called partition columns to separate ternary mixtures. In the case of a partition column, a portion of the column is divided into two subsections by a wall that is arranged in the lengthwise direction of the column. Above and below the partition, the two subsections are connected on the side of the flow in each case. In a corresponding approach, a three-component mixture that is introduced into the subsection on one side of the partition can be separated into three fractions in a single column. The lowest-boiling component can be recovered at the head of the partition column, the middle-boiling component can be recovered on the side of the partition that is opposite to the feed, and the highest-boiling component can be recovered from the bottom. In comparison to a column without a partition, higher concentrations of the middle-boiling component can be achieved with the partition column in the lateral draw-off.

In low-temperature air separation, partition columns have hardly been used to date because of their difficult adjustment. In EP 0 638 778 B1, a process for low-temperature separation of air in a partition column is described. The low-pressure column is divided by a partition in a middle area. On one side of the partition, bottom liquid is fed from the pressure column, while on the other side of the partition, the argon-containing fluid is drawn off. For better adjustment of the process, a waste fluid is removed on the side of

the partition, in which the bottom liquid is introduced. The process parameters are selected such that the recovered argon-containing fluid has an argon concentration of at least 70%.

In the case of a product requirement in the range of 70% argon concentration, the number of theoretical plates in the crude argon column can be reduced with the process described in EP 0 638 778 B1, and thus overall height is saved. If, however, high argon concentrations of, for example, more than 95% are called for, the advantages of a concentration of the fluid that is drawn off from the low-pressure column and fed to the crude argon column to values of above 70% argon are always smaller. The reason for this is that to achieve higher argon concentrations, the majority of the theoretical plates in the crude argon column are necessary to remove the last remnants of oxygen from the argon. That is to say, in the case of high purity requirements, the starting concentration of the fluid that is introduced into the crude argon column plays a lesser role.

The object of this invention is therefore to demonstrate an improved process for recovering argon by low-temperature air separation.

This object is achieved according to the invention by a process of the above-mentioned type, whereby the argon concentration in the stream that is removed in the second subsection is between 15% and 50%, preferably between 15% and 40%, especially preferably between 20% and 35%.

The invention is based on the knowledge that in the case of a specified amount and purity of the argon product, an increase in the starting concentration of argon in the stream that is introduced into the crude argon column entails a reduction of the amount of

vapor that is to be moved. This is positive in as much as the cross-section of the crude argon column is correspondingly reduced, and costs can be saved.

Such an increase in the argon concentration in the lateral draw-off of the air separation column, however, is associated with a complicated design of the air separation column and a more expensive adjustment. It can also be noted that the advantages of the argon concentration in the lateral draw-off from the air separation column are always smaller in the case of high product requirements, since, as described above, in this case the number of theoretical plates in the crude argon column essentially depends on the final concentration to be achieved and not on the starting concentration.

Studies have now shown that the minimum amount of vapor that must be fed to the crude argon column for proper operation first decreases with increasing argon concentration, but remains the same starting from an argon concentration of 50%. That is to say, an additional argon concentration in the lateral draw-off to values of over 50% does not bring any further reduction of the amount of vapor to be introduced into the crude argon column and thus entails no possibility of an additional cross-section reduction of the crude argon column. There remains only the advantage of a higher argon concentration in the mixture that is fed to the crude argon column. Since, however, in the case of high requirements of argon purity, the number of theoretical plates in the crude argon column essentially depends on the starting concentration, a further increase in the argon concentration in the stream that is removed from the air separation column is no longer useful. Within the scope of this invention, this case was examined in more detail, and it was found that an argon concentration of between 15% and 50% in the stream that is removed in the second subsection is especially advantageous.

In practice, it has turned out that an approach in which a stream with an argon concentration of between 15% and 40%, preferably between 20% and 35%, is removed from the second subsection brings special advantages.

The invention is especially advantageous when using a partition column. In this case, the rectifying system has at least one air separation column, which has three rectifying sections that are arranged in series, whereby in each case adjacent rectifying sections can be connected to one another on the gas and liquid sides. The middle rectifying section has a partition that divides the rectifying section into two subsections. Inside the second rectifying section, a gas and liquid exchange between the two subsections is prevented by the partition. Both subsections, however, are connected on the flow side to the rectifying sections located above and below.

Instead of a partition column, the division into two subsections that are flushed in a parallel manner can also be carried out by two columns that are arranged parallel to one another. Liquid is drawn off at an intermediate point for a first air separation column and fed to a second column. Gas is drawn out from the first air separation column at a second intermediate point and introduced into the second column. Gas and liquid, produced at the head of the second column, from the bottom of the second column are returned to the first air separation column, preferably at the two intermediate points. The two subsections that are separated on the flow side are not produced in this embodiment by a partition but rather by two columns that are connected in parallel.

The stream that is removed from the second subsection, either from the air separation column or from the second column, depending on the design, is preferably directed into a crude argon column. The bottom liquid that essentially contains oxygen,

accumulating there, is preferably returned to the second subsection, i.e., in the subsection in which the argon-containing fraction is also removed.

The invention is preferably suitable for a rectifying system, which has a pressure column and a low-pressure column, whereby the partition in the low-pressure column is arranged and whereby a fluid, concentrated with oxygen, from the pressure column, preferably bottom liquid, is introduced into the first subsection.

The advantages of the process according to the invention are shown in particular if argon with a high purity of more than 95%, preferably more than 98%, and/or argon with an oxygen content of less than 100 ppm, preferably less than 10 ppm, is to be recovered in the crude argon column. The invention is then especially advantageous if more than 100 theoretical plates, preferably between 150 and 200 theoretical plates, are used in the crude argon column. In these cases, the overall height of the crude argon column is determined in any case by the number of theoretical plates necessary for the high final purity. The diameter of the crude argon column can be significantly reduced, however, compared to the conventional process without a partition column.

In the air separation column, packings are preferably used for rectification. In this connection, it is advantageous if the packings are arranged in several areas that lie on top of one another, so-called beds, whereby the liquid to be rectified and/or the gas to be rectified are collected between two beds each and redistributed onto the next packing bed. If, instead of packings, other internals or devices are used for rectification in the air separation column, it has also proven of value to provide collectors and/or distributors at specific intervals in the air separation column to be able to counteract poor distribution in the column.

The partition between the two compartmented areas in the air separation column preferably ends in each case on the upper end or the lower end of a packing bed, or when other column internals are used on the upper or lower end of the corresponding area, which is divided from the adjacent area by a collector/distributor. Since, in any case, collectors/distributors are arranged at these points of impact of two column areas, no additional collectors/distributors have to be provided when using the partition. Only the collector/distributor arranged directly above the partition has to be modified, such that it distributes the liquid in the desired way to the two subsections that are divided from one another by the partition. The equivalent holds true if instead of a partition column, a second column that is arranged parallel to the first air separation column is used.

It has proven especially advantageous to divide the air separation column, in particular the low-pressure column of a double column system, into four areas, or when using packings, into four packing beds, and to provide the partition at the level of the second and the third area.

In the first and second subsection, metabolic elements that produce the same pressure drop for the rising gas are preferably used.

The invention as well as additional details of the invention are explained in more detail below based on the embodiments that are depicted in the drawings. In this connection:

Figure 1 shows a device for implementing the process according to the invention,

Figure 2 shows another embodiment according to the invention,

Figure 3 shows the specific amount of vapor to be fed to the crude argon

column based on the argon concentration thereof, and

Figure 4 shows the argon yield based on the argon concentration in the vapor fed to the crude argon column.

In Figure 1, the rectification portion of a low-temperature air separation unit with argon recovery is depicted. After corresponding purification and cooling, charging air 1 is introduced into pressure column 2. The oxygen-concentrated liquid that collects in the bottom of pressure column 2 is conveyed via line 3 into low-pressure column 4.

Low-pressure column 4 is implemented as a partition column. As rectification elements, packings, which are arranged in several beds 19, 20, 21, 22 that are located on top of one another and which in each case have a height of about 6 m, are provided in low-pressure column 4. Between two beds each, collectors/distributors 23, 24, 25, 26, 27 are provided for collecting and distributing the liquid that flows downward in low-pressure column 4.

In a middle area of low-pressure column 4, a partition 5 is arranged, such that low-pressure column 4 is divided into two subsections 6, 7. Partition 5 extends in this case over the entire length of the two middle packing beds 20 and 21. A gas and liquid exchange between the two separate subsections 6, 7 is not possible in this area.

Beds 19 and 22 below and above separate subsections 6, 7 extend, however, over the entire cross-section of low-pressure column 4, such that the gas or liquid streams that separately flow out or flow down into two subsections 6, 7 are merged again.

In compartmented subsection 6, low-pressure column 4 is fed bottom liquid from pressure column 2 via line 3. Moreover, turbine air can be introduced into low-pressure column 4 via line 12. At the head of low-pressure column 4, gaseous product nitrogen

can be recovered via line 8. Also, above compartmented subsections 6, 7, a draw-off 9 for impure nitrogen is provided. Gaseous or liquid product oxygen can be removed from the bottom of low-pressure column 4 via lines 10 and 11.

In two subsections 6 and 7, packings with identical specific surfaces are installed. The vapor that rises in low-pressure column 4 thus experiences the same pressure loss in both subsections 6, 7. The liquid that flows out is distributed in the two subsections 6, 7 by means of distributors 24, 25. The same amount of liquid is preferably released to both subsections 6, 7. To optimize the way the process is performed, however, it may very well be useful to provide different liquid throughputs in subsections 6 and 7. The distribution of the rising vapor to the two subsections 6, 7 is advantageously adjusted automatically based on the amounts of liquid flowing toward it and the pressure losses in packing beds 20, 21.

A stream 13 that essentially contains argon and oxygen with an argon concentration of 35% is drawn off from subsection 7 and introduced into a crude argon column 14 that is provided with packings. In crude argon column 14, the oxygen-argon mixture is rectified. At the head of crude argon column 14, the argon that is produced in a top condenser 15 is condensed and partially recovered as product 16 with a residual oxygen content of less than 10 ppm, and released to portion 17 as reflux liquid in turn to crude argon column 14. In the bottom of crude argon column 14, liquid oxygen, which is fed via line 18 into divided subsection 7 of low-pressure column 4, collects.

In low-pressure column 4, the feeding of bottom liquid 3 from pressure column 2 and turbine air 12 from argon draw-off 13 are separated by partition 5. In this way,

considerably higher argon concentrations can be adjusted in argon draw-off 13 than in columns without partitions.

In Figure 2, an embodiment of the invention is depicted, in which instead of partition 5, a parallel side column 30 is provided. The same elements are provided in both figures with the same reference numbers.

In this case, low-pressure column 4 is designed without a partition. The liquid that flows down from rectification section 22 is distributed, on the one hand, by means of distributor 24 to beds 20, 21, which form the first subsection. The second subsection is produced by side column 30. A portion of the liquid that flows down from packing bed 22 is drawn off via line 31 from low-pressure column 4 and fed to side column 30 at the head. Gas that is produced at the head of side column 30 is returned via line 32 above packing bed 21 into low-pressure column 4. In a corresponding way, liquid from side column 30 is directed via line 33 into low-pressure column 4 or gas from low-pressure column 4 is directed by means of line 34 into side column 30.

The procedures in the embodiments according to Figure 1 and Figure 2 are identical, whereby only in Figure 2, rectifying sections 20, 21 of low-pressure column 4 represent first subsection 6, and side column 30 represents second subsection 7. In a corresponding way, streams 3, 12 are introduced into low-pressure column 4, while argon-containing stream 13 of side column 30 is removed.

Within the scope of this invention, the specific amount of vapor to be fed to crude argon column 14, i.e., the amount of vapor relative to the amount of argon product, was determined by simulations based on the argon concentration of the vapor. The determined dependence is shown in Figure 3. In this case, the process started from an

argon product purity of 98.5% and a constant argon yield, i.e., a constant ratio of argon product to the amount of argon in the charging air.

The solid curve shows the theoretical minimum amount of vapor in the case of a theoretically infinite number of plates. The dotted curve indicates the trace of the conditions calculated for a theoretical plate number of 50. Both curves have essentially the same course. It can be gathered from the curve for the finite plate number, however, that in this case, compared to the theoretical curve, about 30 to 40% larger amounts of vapor have to be used.

Both curves show that first with increasing argon concentration, increasingly less vapor in crude argon column 14 has to be converted to obtain argon of the desired purity and amount. The curves, however, in each case approach a lower boundary value at about 50% argon concentration. In the case of higher argon concentrations, no drop or only a slight further drop of the amount of vapor to be fed is to be expected.

Because of the dropping amount of vapor with the increasing argon concentration in the feed stream to crude argon column 14, the latter can be made correspondingly smaller in its diameter. The reduction of the amount of vapor, however, can be observed only up to an argon concentration of about 50%. With an increase of the concentration to over 50%, however, no further reduction of the amount of vapor can be achieved under the existing conditions, such that also no further reduction in size of the crude argon column cross-section can be achieved. The cost of adjustment associated with the increase in concentration in the low-pressure column increases significantly, however.

Also, the number of theoretical plates in crude argon column 14 cannot be significantly lowered by an increase of the argon concentration in vapor 13 that is to be

fed in the case of a desired product purity of 98.5%, since at high product purities, the number of plates is determined by the final concentration to be achieved and not by the starting concentration.

Low-pressure column 4 is operated, according to the invention, such that in lateral draw-off 13, an argon concentration of 45% is achieved. At this concentration, the amount of vapor that is introduced into crude argon column 14 can be minimized, and the diameter of crude argon column 14 corresponding to the amount of vapor can be reduced.

Figure 4 shows the argon yield based on the argon concentration of the vapor that is fed into the argon column. The solid curve represents the calculated values for a short partition, the dotted curve for a long partition. The plate number in the low-pressure column was kept constant in this case.

On the solid curve, it is shown that the argon yield remains essentially constant in a range of between 10 and 25% argon concentration in the feed vapor. The curve breaks off at 25%, since no higher argon concentrations can be achieved with the partition length used. In the case of a longer partition, upon which the calculation of the dotted curve was based, an essentially constant argon yield can be observed even in the area of higher argon concentrations above 30% up to 90%. An increase in the argon concentration consequently does not have a negative effect on the yield.